

Diffusion controlled degradation analysis of high temperature $(\text{Bi,Sb})_2(\text{Te,Se})_3$ semiconductor thermoelectric power modules

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Abstract

Close-packed array $(\text{Bi,Sb})_2(\text{Te,Se})_3$ compound semiconductor thermoelectric power modules have been used extensively in terrestrial thermoelectric generators for converting thermal energy directly into electricity. In this paper a diffusion controlled degradation model based on a new modified Whipple-type grain boundary diffusion model has been developed. This model considers the effect of temperature gradient on a high diffusivity path and has been developed for studying the degradation mechanism of $(\text{Bi,Sb})_2(\text{Te,Se})_3$ compound semiconductor power thermoelectric modules caused by the formation of dark bands.

Keywords: Thermal diffusion; Thermoelectric devices; Surface diffusion; Defect formation

1. Introduction

The Kadel thermoelectric energy conversion device generally operates at hot junction temperature of 260–316 °C, and maintains temperature gradients of 170 °C between the hot and cold junctions. Owing to the coefficient of thermal expansion mismatch of different parts of the module, thermal stress can occur at the interfaces in the thermoelectric module system during manufacturing and operation. Surface morphology and energy dispersion X-ray spectroscopy studies have shown that edge microcracks, adjacent to the insulator in the semiconductor, propagate along the interphase boundary between the oxidized and non-oxidized areas. This propagation is a result of stress induced impurity diffusion from the microcrack tip to the interphase boundary ahead of the tip. This impurity stress-assisted diffusion cracking involves structural changes that weaken and break the atomic bonds at the interphase boundary zone ahead of the crack tip. Recently, a new dynamic stress assisted diffusion cracking model has been developed for describing the influence of thermal stress on the diffusion rate of the impurity (Fe) ahead of the crack tip and microcrack growth in the brittle $(\text{Bi,Sb})_2(\text{Te,Se})_3$ semiconductor thermoelectric materials [1]. Moreover, electrical

resistance and surface morphology studies further indicate that the high electrical resistance is strongly related to the presence of an oxidized area of semiconductor near the hot junction, which was operated above 260 °C, as well as the dark band along the interphase boundary between the oxidized and non-oxidized areas of the P type semiconductor thermoelements. The formation of the dark band is caused by surface diffusion of impurity atoms from the insulator (separator) into the microcrack which propagate along the interphase boundary inside the semiconductor. A schematic diagram and scanning electron micrograph showing the dark band are illustrated in Fig. 1. The major goal of this study is to investigate the mechanism of diffusion controlled dark band formation on a common phenomenological basis. Mostly, surface diffusion of impurities along the microcrack (such as Si with low diffusivity) can be logically modeled by the same approach used for grain boundary diffusion. Accordingly, the formation of the dark band due to the surface diffusion along the microcrack high diffusivity path can be successfully modeled by a new modified Whipple-type grain boundary diffusion solution which takes into account the effect of temperature gradient driving force on grain boundary diffusion. A geometric model for grain

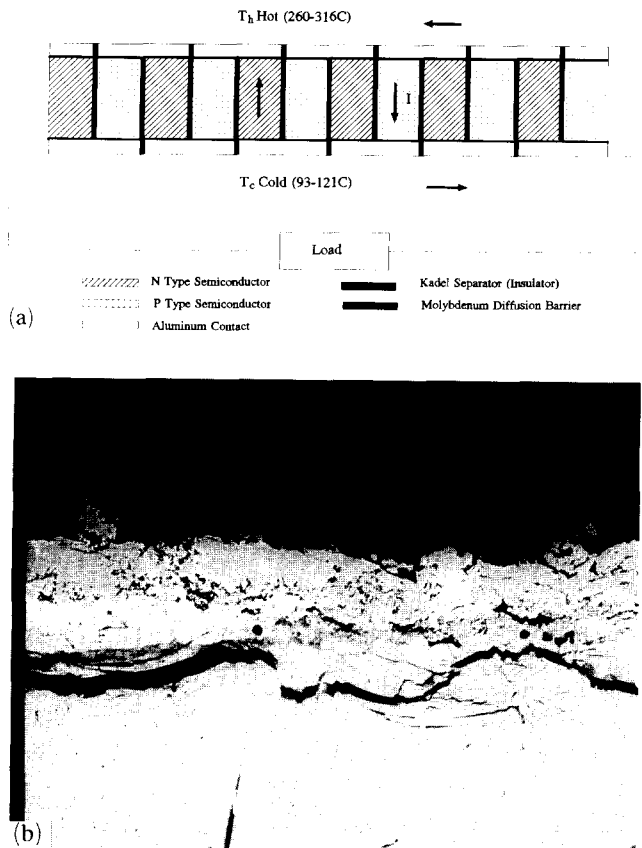


Fig. 1. Kadel thermal electric module: (a) schematic diagram of the power thermoelectric module and generator and (b) scanning electron micrograph showing the dark band in the semiconductor thermoelement.

boundary diffusion in the thermoelectric module with a microcrack, which is treated as a grain boundary, is shown in Fig. 2.

2. Physical model and equations

Based on the linear diffusion theory, the flux with a solid state thermomigration driving force can be expressed [2] as

$$J = -D \left(\nabla C - \frac{CF}{KT} \right) \quad (1)$$

where D , C , F and k represent the diffusivity, concentration, thermomigration driving force and Boltzmann's constant respectively.

Finite element calculation has shown that the temperature profile for $(\text{Bi, Sb})_2(\text{Te, Se})_3$ semiconductor thermoelectric power modules can be treated reasonably as linear in the dark band [3]. Therefore, the driving force for thermal diffusion can be written [4]

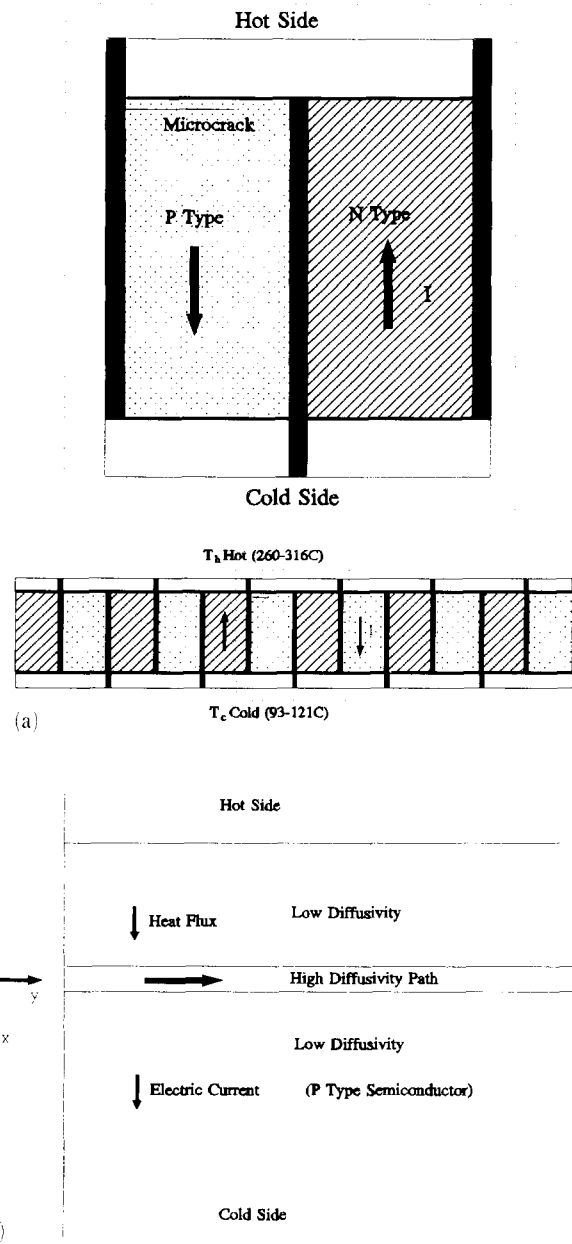


Fig. 2. Schematic illustration of (a) location of microcrack in the Kadel thermal electric module and (b) geometric model for grain boundary diffusion in the thermoelectric module with the microcrack as a high diffusivity path.

$$F = -\frac{Q^*}{T} \frac{dT}{dx} = -\frac{Q^*}{T} \frac{\Delta T}{\Delta x} \quad (2)$$

where Q^* is the heat of transport and dT/dx is the temperature gradient. Then the diffusion with the driving forces becomes

$$\frac{\partial C}{\partial t} = D \nabla^2 C - \frac{DF}{KT} \nabla C \quad (3)$$

Our approach to the diffusion problem is similar to that used by Whipple [5]. In this paper, a two-dimensional grain boundary diffusion model influenced by a thermomigration driving force is taken into account. This driving force is perpendicular to the microcrack. Let the concentration and diffusivity within the high diffusivity path be given by $C_2(x, y, t)$ and D_2 and the drain into the adjacent lattice by $C_1(x, y, t)$ and D_1 . The width of the high diffusivity path is δ . D_1 and D_2 are logically assumed to be constant and the temperature gradient independent within the very narrow dark band. The diffusion equations with the perpendicular thermal gradient driving force can be expressed as

$$D_1 \left(\frac{\partial^2 C_1}{\partial x^2} + \frac{\partial^2 C_1}{\partial y^2} \right) - \frac{D_1 F_1}{KT} \frac{\partial C_1}{\partial x} = \frac{\partial C_1}{\partial t} \quad |x| > \frac{\delta}{2}$$

$$D_2 \left(\frac{\partial^2 C_2}{\partial x^2} + \frac{\partial^2 C_2}{\partial y^2} \right) - \frac{D_2 F_2}{KT} \frac{\partial C_2}{\partial x} = \frac{\partial C_2}{\partial t} \quad |x| < \frac{\delta}{2}$$
(4)

where F_1 and F_2 are the effective driving forces in the lattice and at high diffusivity path, respectively.

Assume that the concentration and flux are continuous at the interface between the boundary and the lattice ($x = \pm \delta/2$), and that the surface concentration maintains constant value C_0 .

$$C_1 = C_2 \quad (5)$$

$$D_2 \frac{\partial C_2}{\partial x} = D_1 \frac{\partial C_1}{\partial x} \quad (6)$$

Rearranging terms and ignoring terms of the order of δ^2 , the new governing equations become

$$\frac{\partial C}{\partial t} = D_1 \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right) - \frac{D_1 F_1}{KT} \frac{\partial C}{\partial x} \quad |x| > \frac{\delta}{2}$$

$$\left(\frac{D_2}{D_1} - 1 \right) \frac{\partial C}{\partial t} = D_2 \frac{\partial^2 C}{\partial x^2} - \frac{2D_1}{\delta} \frac{\partial C}{\partial x} + \left(\frac{D_1 F_2}{KT} - \frac{D_2 F_1}{KT} \right) \frac{\partial C}{\partial x} \quad |x| = \frac{\delta}{2}$$
(7)

where C represents the total lattice concentration which is due to ordinary diffusion in the lattice and diffusion out from the high diffusivity path to the lattice. Eq. (7) is subjected to the initial and boundary conditions as given by

$$C(x, 0, 0) = C_0 \quad C(x, y, 0) = 0$$

$$C(x, 0, t) = C_0 \quad C(\infty, \infty, t) = 0$$
(8)

and can be solved by means of Fourier–Laplace transform.

Consequently an exact solution, taking into account the effect of thermal gradient driving force, can be written

$$C(x, y, t) = C_l(x, y, t) + C_h(x, y, t)$$

$$C(x, y, t) = C_0 \operatorname{erfc} \frac{\eta}{2} + \frac{C_0 \eta}{2\sqrt{\pi}} \int_1^{\Delta} \frac{d\sigma}{\sigma^{3/2}} \exp -\frac{\eta^2}{4\sigma}$$

$$\times \operatorname{erfc} \left\{ \frac{1}{2} \left(\frac{\Delta - 1}{\Delta - \sigma} \right)^{1/2} \left[\xi + \frac{\sigma - 1}{\beta} + \frac{\sigma - 1}{\Delta - 1} \right] \right\}$$

$$\times \left(\frac{D_2 F_1 - D_1 F_2}{KT} \right) (D_1^{-1/2} t^{1/2}) \quad (9)$$

with dimensionless parameters

$$\xi = \frac{x - (\delta/2)}{(D_1 t)^{1/2}}$$

$$\eta = \frac{y}{(D_1 t)^{1/2}}$$

$$\Delta = \frac{D_2}{D_1}$$

$$\alpha = \frac{\delta}{2(D_1 t)}$$
(10)

$$\beta = (\Delta - 1)\alpha$$

where C_l is the lattice concentration owing to planar lattice diffusion in the absence of the high diffusivity path contribution, C_h is the lattice concentration owing to out-diffusion from the high diffusivity path, erfc is the complementary error function and σ is the integration variable.

3. Discussion

The effect of the driving force caused by the temperature gradient on grain boundary diffusion becomes evident by comparing Eq. (9) with Whipple's solution. In C_l , the η dependence in the complementary error function remains unchanged. Hence the driving force caused by temperature gradient perpendicular to the high diffusivity path has no effect on the contribution to C_l from direct volume or lattice diffusion. Lattice diffusion owing to out-diffusion from the

high diffusivity path C_h is explicitly modified along the x -direction parallel to the driving force by the term

$$\chi = \frac{\sigma - 1}{\Delta - 1} \left(\frac{D_2 F_1 - D_1 F_2}{K T} \right) (D_1^{-1/2} t^{-1/2}) \quad (11)$$

in a complementary error function. While atomic flow across the high diffusivity path is more sensitive to temperature gradient than in the lattice, F_2 is larger than F_1 . In addition, the diffusivity of impurity within the high diffusivity path D_2 is much larger than inside the lattice or volume D_1 , so that $D_2 F_1$ is larger than $D_1 F_2$. Substituting Eq. (2) into (11), the shifting term χ in the complementary error function of C_h is given by

$$\chi = \frac{\sigma - 1}{\Delta - 1} \left(\frac{D_1 Q_2^* - D_2 Q_1^*}{K T^2} \frac{\Delta T}{\Delta x} \right) (D_1^{-1/2} t^{1/2}) \quad (12)$$

where Q_1^* is the heat of transport in the lattice and Q_2^* is the heat of transport in the high diffusivity path. Note that $Q_2^* > Q_1^* > 0$ and $D_2 Q_1^* > D_1 Q_2^*$, which indicate that the shifting term χ in the argument of the complementary error function (erfc) is negative. Consequently, the decrease in the argument of the erfc term owing to the negative shifting term χ enhances impurity lattice penetration from the high diffusivity path into the non-oxidized area below the microcracks treated as the high diffusivity path. Alternatively, an increase in the argument of the erfc term owing to the positive shifting term χ diminishes the impurity lattice penetration from the high diffusivity path into the oxidized area above the microcrack. However, the overall lattice composition profile is adjusted by the shifting term along the direction of thermomigration. It is worth noting that the formation of the dark band caused by redistribution of impurities along the microcrack (high diffusivity path) and in the matrix (lattice) of the semiconductor is influenced not only by the temperature gradient (thermomigration), but also by the electric current (electromigration) in the direction normal to the high diffusivity path. Electromigration

may reinforce or counteract formation of the dark band, which depends on the direction of electric current and the type of semiconductor (N- or P-type) involved.

4. Conclusions

This diffusion degradation model is in good agreement with the dark band observed in the brittle $(\text{Bi}, \text{Sb})_2(\text{Te}, \text{Se})_3$ thermoelements. There is a strong correlation between the temperature gradient driving force and the formation of a dark band that degenerates the thermoelectric power and increases the electrical resistance of the thermoelectric module. A thermomigration driving force enhances penetration of impurities into semiconductor thermoelements and accelerates the rate of performance degradation. This model considers the effect of the thermomigration driving force perpendicular to high diffusivity path and may also be applicable to ceramic materials with temperature differences between the surface and interior regions owing to poor thermal conductivity.

Acknowledgments

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